ISOTOPE SEPARATIONS

Gas Centrifugation

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Introduction

The idea that a centrifugal field might be used to separate was first suggested by Lindemann and Aston in 1919. In 1934 Beams and others at the University of Virginia developed a convection-free centrifuge for isotope separations, shown in **Figure 1**. Two years later Beams and Haynes demonstrated practical separation of chlorine isotopes. In 1938 the Nobel prize winner Urey suggested multiplying the separating effect between axis and periphery of a rotor produced by centrifugal forces by introducing countercurrent convection (like a fractionating column) within the spinning tube. At the end of the 1930s Groth and co-workers in Germany started to construct a high speed centrifuge for uranium isotope separation with axial countercurrent flow induced

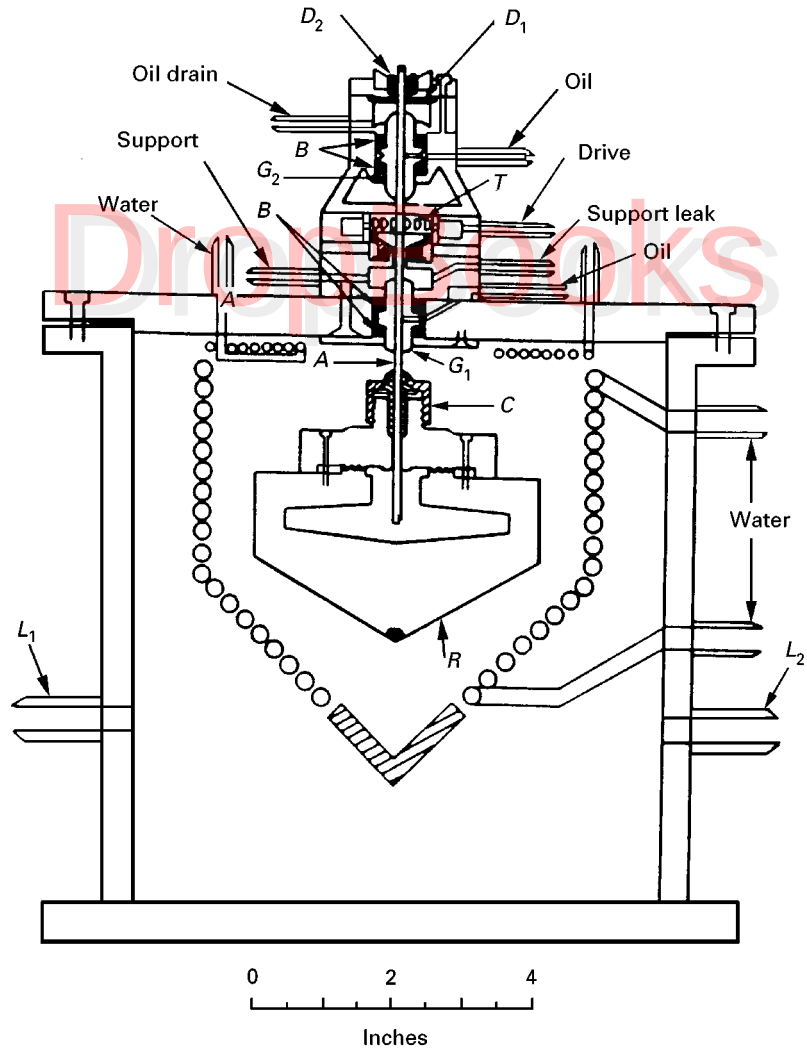

Figure 1 Schematic drawing of Beams' first successful evaporative centrifuge used to separate chlorine isotopes.

by heating the bottom of a rotor and cooling the top.

With the beginning of the Second World War in 1939, the separation of uranium isotopes became a subject of national importance. The experimental work on developing different types of gas centrifuges for uranium isotope separation was continued in Germany and was undertaken in the USA in the framework of the Manhattan Project. In that time, Dirac made fundamental contributions to the theory of the isotope separation process in a gas centrifuge, and Onsager's theory for calculation of separation efficiency in a thermal diffusion column was generalized for gas centrifuges by Cohen in 1951. They and their colleagues worked out a general mathematical model and demonstrated theoretically the ideal countercurrent flow profile to produce the maximum separation efficiency. Beginning in 1946, Steenbeck and Zippe contributed to the centrifuge development project in the USSR. Together with Russian co-workers, they developed a very elegant bearing system and adapted the scoop system of gas extraction not only to recover the gas from the rotor but also to generate the circulation flow to multiply the radial separating effect. After leaving the USSR in the mid 1950s, Zippe continued his activities in Germany and USA to reproduce the experiments that had been performed in USSR. In the USA, Zippe worked with Beams for about 2 years in the late 1950s. The Virginia short-bowl centrifuge, similar to the Russian design, was the result of their collaboration. A research and development programme for centrifugation was then pursued in the USA with the central effort located at the Department of Energy laboratories at Oak Ridge, Tennessee. In this programme, centrifuge rotors of an unprecedented length, of the order of 13 m were developed. The programme proved to be technically successful, but it was terminated in 1985 because of changes in US nuclear policies.

After the Second World War, centrifuge research programmes were initiated in several other countries: in the UK by Kronberger and Whitley; in France by Burgain and Le Manach; in Germany by Beyerle, Groth and Martin; in the Netherlands by Kistemaker and Los; in Japan by Kanagawa, Oyama and Takashima; and in Sweden by Landahl and associates.

The Soviet Union was the first country where this technology was developed on an industrial level. The first pilot plant, comprising 2500 gas centrifuges, was put into operation in 1957. The first industrial plant, which contained several tens of thousands of centrifuges, was commissioned in 1959. Soon after, USSR built an industrial plant with several hundred thousand centrifuges configured in three levels and commissioned it in 1962–1964. Besides Russia, this method was commercialized at the end of the 1970s by the UK, Germany and the Netherlands collaborating and in the 1980s by Japan. At present, gas centrifugation is the most efficient, economic and reliable technology for production of enriched uranium.

Principles of Operation

The history of the development of a gas centrifuge for uranium isotope separation provides an excellent example of successfully overcoming numerous experimental and theoretical problems in the fields of physics of separation processes, gas dynamics, materials science, mechanical engineering and physical chemistry. The short-bowl centrifuge patented in 1957 by Zippe, Scheffel and Steenbeck is shown in **Figure 2**. The thin-walled vertical cylindrical rotor is suspended at the bottom by a low friction needle bearing and at the top by a frictionless magnetic bearing. It also uses damping bearings to resist vibrations at both ends of the rotor. In the case of the separation of uranium isotopes, uranium hexafluoride (UF_6) is introduced into the spinning rotor from a stationary central post and removed from stationary pipes called scoops located at either end of the

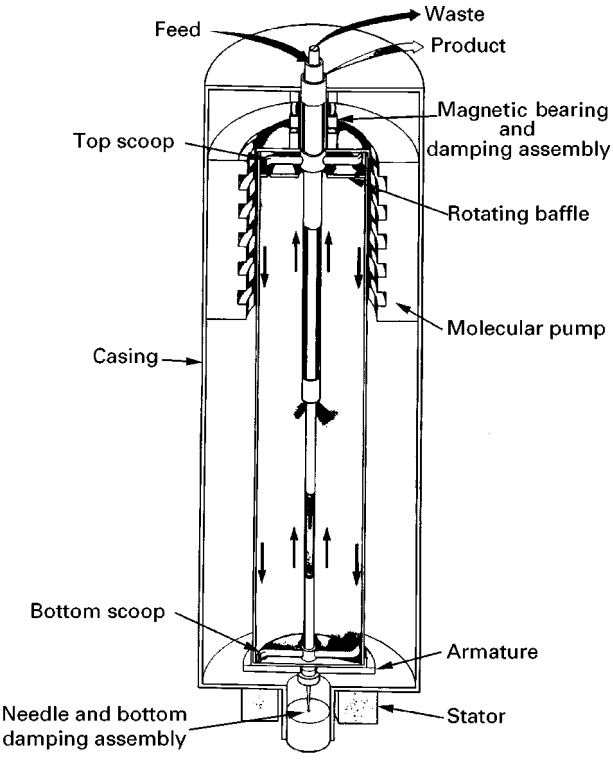

Figure 2 Schematic drawing of Zippe-type centrifuge.

rotor. In practice, the gas centrifuge is spun in a vacuum housing that is maintained by a Holweck-type spiral groove molecular pump. The very high peripheral speeds (for example, in the order of 600 m s^{-1}) generate centrifugal forces that compress the process gas into a thin stratified layer adjacent to the cylindrical wall of the rotor.

Separation Factor

The action of centrifugal forces causes a partial separation of isotopes along the rotor radius. If we consider the process gas to be a binary mixture of the two isotopic species $^{235}UF_6$ and $^{238}UF_6$, then the heavier molecules containing $^{238}UF_6$ will tend to be concentrated near the cylinder wall and the lighter molecules containing $^{235}UF_6$ will tend to be concentrated near the axis. Considering UF_6 as an ideal gas, a pressure gradient is developed which is governed by eqn [1]:

$$\frac{dp}{dr} = \frac{Mp}{RT}\omega^2 r \qquad [1]$$

Here p is the pressure, M is the molecular weight of the gas, R is the gas constant, T is the absolute temperature, ω is the angular frequency of rotation and r is the radial coordinate. In the case of an isothermal centrifuge, the equation above is readily integrated to yield the following relation:

$$p(r) = p(0)(M\omega^2 r^2/2RT) \qquad [2]$$

that gives the pressure $p(r)$ at any radial position r in terms of the pressure at the axis $p(0)$. For a mixture of two ideal gases of molecular weights, M_1 and M_2, each gas would have a pressure governed by eqn [2] and the ratio of the two pressures gives the radial separation under equilibrium conditions (i.e. no axial gas circulation). An equilibrium separation factor between the two gases is therefore given by the expression:

$$\alpha_0 = \frac{x_1(0)}{x_2(0)}\Big/\frac{x_1(a)}{x_2(a)} = \exp[(M_2 - M_1)\omega^2 a^2/2RT] \qquad [3]$$

in which x_1 and x_2 are the concentrations of species 1 and 2, respectively, and a is the radius of the rotor.

The fundamental advantage of this technique over many other diffusion separation methods is that the primary isotope separation effect occurs at thermodynamic equilibrium. It should also be noted that the separation factor for the centrifuge process is a function of the absolute difference in the molecular weights of the components being separated. This is in contrast to various diffusion separation processes where it is a function of the ratio of the molecular weights.

Separative Capacity

The stationary scoop at the top of the rotor induces a countercurrent flow by removing both mass and angular momentum, which induces pumping of the gas radially inward, forcing it to travel down near the axis and up along the cylinder wall. In order to prevent the influence of the scoop at the bottom, it is shielded by a baffle that rotates with the rotor and has holes which allow the gas to enter the scoop chamber and be removed from the centrifuge. This countercurrent flow produces a net transport of heavy isotopes to the top of the rotor and a net transport of light isotopes to the bottom, establishing a concentration gradient in the axial direction that is considerably greater than the primary (radial) isotope separation effect. Therefore, the gas removed by the bottom scoop is enriched in $^{235}UF_6$ (a product stream) and the gas removed by the top scoop is depleted in $^{235}UF_6$ (a waste stream).

As manufacturing technology has improved, higher rotational speeds have been achieved to obtain greater separation performance. At these higher speeds, shock waves develop in front of the stationary scoop, and the temperatures associated with these shock waves are high enough to cause decomposition of the process gas. It is important to note that the speed of sound in UF_6 at room temperature is approximately 90 m s^{-1}, and the peripheral speed of rotation of the process gas in modern centrifuges can be more than seven times greater than this. One design that avoids this decomposition problem is to shield the upper scoop with a rotating baffle with two concentric systems of holes. One system is located near the periphery to allow gas to enter the scoop, and the other system is located nearer the axis of rotation to induce internal circulation. Again, this internal circulation creates an axial separation factor many times that of the basic radial separation factor. The design of scoops and systems of holes in both baffles (their position and size) together with the temperature distribution on the side wall are used to control the internal circulation value and rate.

In 1941, Dirac demonstrated that a gas centrifuge, no matter how it is operated, has the maximum theoretical capacity:

$$\delta U_{max} = \rho D\left(\frac{\Delta M\omega^2 a^2}{2RT}\right)^2 \pi Z/2 \qquad [4]$$

where Z is the length of the rotor, ΔM is the difference in molecular weights, ρ is the density of the

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Table 1 Maximum pressure ratio, radial separation factor and separative work at various peripheral speeds

ωa ($m\,s^{-1}$)	$p(a)/p(0)$ for $^{235}UF_6$	α_0	δU_{max} kg SW per year	L/a^a
300	573	1.056	2.15	Does not exist
400	8×10^4	1.101	6.78	0.571
500	4.6×10^7	1.162	16.55	0.309
600	1.1×10^{11}	1.242	34.32	0.202
700	1.0×10^{15}	1.343	63.59	0.144

[a] L/a: Ratio of radial distance for pressure to fall by 10^4 to centrifuge radius.

process gas, D is the coefficient of self-diffusion, and δU is the separative capacity in moles per unit time. Maximum pressure ratio, radial separation factor and separative work at various peripheral speeds of a gas centrifuge are presented in **Table 1**.

Design Principles

As is evident from eqn [4], the most important parameters in centrifuge technology are peripheral rotor speed and rotor length. The peripheral speed is limited by the strength of the rotor material. Hence, gas centrifuges require materials which have a high strength to density ratio. Such materials are aluminium alloys, titanium alloys, alloy steels or fibre composites. The centrifuge rotor can be made of more than one layer; for example, aluminium alloy covered with fibre composites. The materials problems include long-term fatigue and creep at high speeds. Because uranium hexafluoride forms hydrofluoric acid even with only a little moisture, corrosion is also a challenging problem area that must be addressed in the design.

The spinning rotor has certain natural frequencies determined by the materials of construction, the rotor length to diameter ratio, and the damping characteristics of the suspension systems. Centrifuges that operate at rotational frequencies below the lowest natural flexural frequency of the rotor are called subcritical centrifuges, and those that operate at rotational frequencies above the first natural frequency are called supercritical ones. As a rule, the rotors of supercritical machines consist of sections connected by bellows that act to reduce vibrations caused by resonant frequencies at certain operating speeds.

The Dirac maximum separative capacity has been derived for the case of an ideal circulation profile in a gas centrifuge. However, this ideal profile cannot be achieved in practice. The flow patterns that actually occur within a centrifuge rotor are governed by the equations of fluid dynamics. The theoretical solution of these equations provides a basis for the optimization of the internal flow pattern that yields the maximum separation performance of a particular gas centrifuge design.

The flow pattern in a gas centrifuge can be divided into three regions in the radial direction, each with different flow features. Near the side wall, the flow is dominated by viscosity, and a strongly rarefied gas region (a vacuum core) is located near the axis of rotation. These two regions are connected by a transition region. The transition region as a rule occupies only a few per cent of the rotor radius, and its influence on separation is negligible. The vacuum core in modern centrifuges is spread over approximately three-quarters of the rotor radius. In this region the mean free path of the gas molecules is comparable with the rotor diameter. At these low pressures, the central core of the rotor cannot contribute to the isotope separation. As a result, the separation power of a gas centrifuge at high speeds increases only as the square of the peripheral speed instead of the fourth power, as given by the Dirac equation.

Cascade of Centrifuges

The separative work output of a single gas centrifuge is generally small compared to the total desired separative work. Hence, it is necessary to combine many centrifuges into a cascade to achieve the desired separation. Each stage of a cascade may have many centrifuges connected in parallel. This arrangement of the large number of centrifuges allows for simple replacement of a faulty individual centrifuge in the cascade. The considerable advantage of the centrifuges is that they need no special compressors for pumping gas through the cascade. The pressure difference required for pumping the gas through the cascade is generated by the dragging action of the scoops on the rotating gas. The cascade contains only centrifuges and piping. Thus, gas centrifuge enrichment of uranium uses only about 1/20th to 1/30th of the electricity per unit of separative work required by the gaseous diffusion process. The reliability of modern centrifuges allows them to operate nonstop for more than 15 years with a failure rate of only a few tenths of 1% per year. Once put into operation, gas centrifuges require no special preventive maintenance through their service lives, and the machines' separation characteristics remain practically constant over time. Provided that random failures occur, the fragments of the crashed machines can be left in the cascade because they will not have much effect on the overall cascade efficiency.

Separation of Nonuranium Isotopes

New Scientific Problems

More recently, interest has been shown in using gas centrifuges for other kinds of separations like stable isotopes or the isotopes of spent reactor uranium. For the stable isotopes, demand is growing in medicine and fundamental physics research, and the use of the gas centrifuge process makes it possible to produce isotopes economically when large (kilograms) quantities are needed. This is the case for the isotopes of xenon, krypton, tungsten, molybdenum, iron, tin, tellurium, sulfur, silicon, germanium, chromium and many others. The separation of stable isotopes by gas centrifuge has been underway for more than three decades in Russia. Currently, cascades of thousands of centrifuges are producing tens of kilograms of various isotopes. In another application, some countries have considered gas centrifuge technology as part of the reprocessing cycle of the re-enrichment of the spent uranium from power reactors which contains five isotopes: U^{232}, U^{234}, U^{235}, U^{236} and U^{238}.

A centrifuge designed for binary separations with uranium hexafluoride cannot be efficiently used for nonuranium isotope separation with different chemical compounds. Therefore, centrifuges with specific characteristics must be designed for particular separation problems. For some isotopes, specially synthesized gaseous chemical compounds must be prepared for use as the process gas. The basic condition for the applicability of the process gas in these newly designed centrifuges is that the gas vapour pressure is not less than 5–10 mmHg under normal operating temperatures. In addition to the condition that this substance should not corrode the structural material of the centrifuge, it has to be sufficiently resistant to temperature dissociation, and preferably must possess the maximum possible content of the desired element in the molecule. The list of such substances includes fluorides and oxyfluorides of metals and nonmetals, metal–organic and complex compounds, phosphorus hydrides, boron hydrides, Freons and some others. Significant differences in the chemical and physical properties of process gases leads to the necessity to create a set of gas centrifuge designs for various ranges of molecular masses. The internal circulating flow must be optimized for each of these designs.

The synthesis of volatile compounds suitable for process gases was not the only scientific problem the researchers faced when separating nonuranium isotopes. In contrast to natural uranium, most chemical elements are polyisotopic. This property leads to additional difficulties in enriching the intermediate components of the isotope mixture.

As perhaps the greatest achievement in the development of centrifuge technology for enrichment of nonuranium isotopes, one may consider the complex isotope separation for iron, carbon and oxygen as a pentacarbonyl of iron – $Fe(CO)_5$. This separation has been realized on an industrial scale at the electrochemical plant in the Krasnoyarsk region of Russia. All chemical elements included in the molecule structure are polyisotopic: iron contains four, carbon two, and oxygen three isotopes. A natural isotope abundance of $Fe(CO)_5$ represents a mixture of 284 types of molecules with different isotope distributions. These types are distributed through 20 components with molecular masses from 194 up to 213. Almost every one of them contains several isotopes for each of the chemical elements. This isotopic overlapping of iron isotopes with intermediate masses and heavy isotopes of carbon and oxygen limits the direct enrichment by a centrifuge cascade. However, this limitation has been removed by introducing into the separation process the isotope exchange between the molecules of pentacarbonyl of iron in so-called photoreactors. The combination of isotope separation in gas centrifuges with isotope exchange has allowed the achievement in a single process of a complex mix of highly enriched isotopes: ^{57}Fe with concentration more than 99%, ^{13}C and ^{18}O with concentrations up to 80%.

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Advantages

The accumulated experience in separating isotopes of both light (boron, carbon, nitrogen and oxygen) and heavier chemical elements has shown gas centrifuge technology to be extremely promising. At the moment, isotopes of more than 20 chemical elements have been separated by gas centrifuges. The centrifuge cascade used for the separation of nonuranium isotopes usually has very low energy consumption and tens of times higher productivity than that of the electromagnetic installation and with a comparable output (**Figure 3**). Nonuranium isotope separation has been transformed into an independent area for development of gas centrifuge technology. It includes solving problems in the design of different types of centrifuges, in the theory of multicomponent isotope mixture separation, in chemical synthesis of process gases, in transformation of process gases with enriched isotopes required for use in chemical compounds, etc.

In many applications of isotope enrichment, rigid requirements on the isotope purity must be met, and undesired gas impurities must be reduced to a specified level. Gas centrifugation has also been recommended as an excellent practical tool to clean small

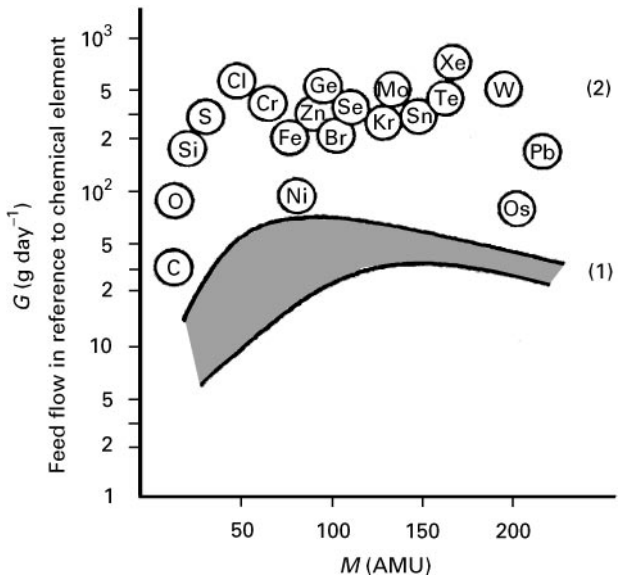

Figure 3 Illustration to compare the separation of nonuranium isotopes by electromagentic separation (1) and by gas centrifuge (2). Production, G (g day^{-1}: feed flow into the installation), versus molecular mass, M, of the separating chemical element. Reproduced with permission from Goldstein *et al.* (1993).

gas impurities. An extremely important benefit of gas centrifuges is the opening of an era of economical large scale production of many stable isotopes that have applications in medicine, industry and fundamental science. For example, experiments on neutrino physics with large detectors that require tens of kg of enriched isotope have been made possible by the cost reductions achieved through the large scale production by gas centrifugation.

Future

The gas centrifuge is now a mature technology, but nevertheless the development potential has not been exhausted. The separation efficiency of existing gas centrifuges for separation of uranium and nonuranium isotopes can be further improved. Additionally, the technology can be applied in the near future to the re-enrichment of uranium from spent nuclear fuel as well as to enriching tails (depleted uranium of separating plants) to the natural isotopic concentration or higher. In yet another area, experiments have been performed which show promising results for the application of gas centrifuge technology to purification of process gas from aerosol particles that can be used, for example, in the semiconductor industry.

See Colour Plate 102.

Further Reading

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Liquid Chromatography

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Introduction

The application of isotopes in science and especially in analytical chemistry is based on two rather contradictory assumptions. Tracer experiments require that the isotopically modified and unmodified compounds behave in a very similar manner. A study of isotope effects must recognize, measure and interpret minute differences in the chemical and physical properties of compounds (isotopomers) that differ in their isotopic composition. These differences lead to different behaviour of isotopomers in all chromatographic processes, as has been demonstrated experimentally.

As early as 1938, Urey and coworkers published a paper on enrichment of ^{6}Li by ion exchange